Glass and Ceramics, Vol. 68, Nos. 3 – 4, July, 2011 (Russian Original, Nos. 3 – 4, March – April, 2011)

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.291.5

SILICA BASED PIGMENTS

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Translated from *Steklo i Keramika*, No. 3, pp. 3 – 7, March, 2011.

Research on the synthesis of ceramic pigments using silica gel and quartz sand is presented. It has been determined that the temperature of synthesis and the composition are related with the properties of the pigments. It is shown that the pigments are best obtained using quartz sand. A wide palette of pigment colors was obtained by introducing transition-metal oxides (CoO, NiO, Fe_2O_3, Cr_2O_3), mineralizers (H_3BO_3, Na_2CO_3, NaF), and modifiers (ZnO, CaO, MgO).

Key words: pigment, silica, oxides, mineralizers, color characteristics, synthesis.

This work concerns the synthesis of differently colored chemically stable ceramic pigments using quartz and silica gel, intended for decorating glazed earthenware and porcelain articles and other types of ceramics, glass, and silicate binding materials.

Stringent requirements with respect to purity and constancy of the chemical composition are imposed on the initial materials used for obtaining ceramic pigments. In the present work, natural minerals such as enriched quartz sand from the Gomel' Ore-Enrichment Works and silica gel, which meet these requirements, were used as the initial materials to synthesize ceramic pigments.

Transition metals are most often the chromophores in ceramic pigments. These elements are characterized by an unfilled electronic shell and possess high polarizability. Their color depends on the polarizability of the ion, specifically, oxygen, present in the complexes: $[CoO_4]$, $[CoO_6]$, $[NiO_4]$, $[NiO_6]$, and $[CrO_4]$. The anions of these complexes polarize the cation, shifting the absorption band of the pigments into the visible region of the spectrum.

Chromophoric ions such as Ni^{+2}, Cr^{+3}, Co^{+2}, Fe^{+3}, and others can participate in the synthesis process and the formation of new phases. In this connection, initial components which affect the color characteristics make it possible to obtain a more diverse palette of pigments.

The 3*d* transition-element oxides CoO, NiO, Fe_2O_3, and Cr_2O_3 were used as chromophores and ZnO, CaO, and MgO as modifiers. Mineralizers play a special role in obtaining pigments which have high chromophoric properties and which are synthesized at low temperatures. In our case these were H_3BO_3, Na_2CO_3, and NaF [1 – 3].

The initial materials named above made it possible to synthesize pigments with different structure and a wide color palette.

Silica gel, which is a waste product of the chemical production of fluorine salts, specifically, aluminum fluoride, can be used together with natural quartz in the initial mix to synthesize pigments. The impurities Al^{3+} and F^- present in silica gel prevent its use as a silica-containing component without preliminary purification. The main secondary components of silica gel are $Al(OH)_3$, AlF_3, and H_2SiF_6. The chemical composition of silica gel (mass content, %) are: 23 – 30 SiO_2; 2 – 20 Al_2O_3; 50 – 70 H_2O; Al_2O_3 — no more than 2%; 0.07 – 0.3 F^-; 1.63 – 14.85 $Al(OH)_3$.

The pigment mixes were prepared by carefully comminuting and mixing the powders of the initial components, chromophore oxides, and modifiers.

The pigments were synthesized in an electric furnace at temperatures 1000 ± 20, 1100 ± 20, and 1200 ± 20°C with soaking for 1 h at the maximum temperature.

The pigments calcined at lower temperatures possessed lower chromophoric properties, which showed that the amount of the color-carrying phase formed was inadequate.

The compositions of the pigments based on silica gel and their color as functions of the calcination temperature are presented in Table 1. The color of the synthesized pigments was assessed visually.

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0361-7610/11/0304-0071

TABLE 1. Composition and Color of Pigments

Composition	Pigment mix composition, %*					Color of pigments calcined at temperature, °C		
	Silica gel	CoO	NiO	Fe_2O_3	Cr_2O_3	1000 °C	1100 °C	1200 °C
1	95	5	–	–	–	Very pale blue	Pale blue	Deep blue
2	90	10	–	–	–	Same	Deep blue	Deep blue
3	85	15	–	–	–	Pale blue	Same	Same
4	95	–	5	–	–	White light green	White	White
5	90	–	10	–	–	Very pale green	Very pale green	Light green
6	85	–	15	–	–	Light green	Light green	Deep light green
7	95	–	–	5	–	Pale beige	Beige	Beige
8	90	–	–	10	–	Beige	Same	Same
9	85	–	–	15	–	Light brown	Brown	Deep brown
10	95	–	–	–	5	Light green	Green	Deep green
11	90	–	–	–	10	Same	Same	Same
12	85	–	–	–	15	Green	Deep green	″

* Content by weight.

Visual examination of the pigment color showed that as the synthesis temperature increases, the color of the calcined samples intensifies, which, evidently, is due to the type and amount of the color-carrying phases formed and the adsorption indications of the chromophore ions on the surface of the pigment particles. New color-carrying phases of the predominately orthosilicates are formed during synthesis of the pigments.

The mineralizers increase the possibility of this embedding because of the appearance of a liquid phase, creating artificial centers of crystallization of phases, and formation of color-carrying phases.

On heating the boric acid H_3NO_3 is dehydrated and transforms into metaboric acid and then into glassy boron oxide. In many cases boron oxide has a positive effect on the chromophoric properties of the pigments. For example, it was found that the chromophoric properties of the synthesized pigments are manifested most strongly when orthoboric acid is present in the pigment mixes.

It is known that as a result of isomorphic substitution of cations in the crystalline structure modifying additives intensify solid-phase sintering.

As a result of visual assessment of the color of the synthesized pigments the compositions 3, 6, 9, and 12, into which modifying oxides were introduced, were chosen as optimal. The colors of the pigments studied, which were calcined at 1200°C, are presented in Table 2.

The pigments colored by Ni(II) oxide are characterized by a light pale green color, which as the synthesis temperature increases, becomes a saturated light green color. Such a color of the synthesized nickel-containing pigments is probably due to the tetrahedral coordination of the nickel (II) ion and is explained by photon absorption.

The chromophoric properties of the synthesized pigments were evaluated using the results obtained from spectral reflection using an electronic spectrophotometer and the SF-18 spectrophotometer which automatically recorded the reflection spectra in the wavelength range 400 – 750 nm. It was found that the reflection coefficients of pigments with the optimal compositions, calcined at 1200°C, are quite high (80 – 90%), which corresponds to light tones with low saturation.

The color coordinates and the dominant wavelength were calculated for pigments with the optimal compositions. The results are presented in Table 3.

TABLE 2. Color of Pigments Containing Modifiers

Modifier	Color of pigment with composition			
	3	6	9	12
ZnO	Gray light blue	Light green	Dark brown	Deep green
CaO	Light blue	Deep light green	Same	Pale green
MgO	Very pale blue	Same	Pale brown	Same

TABLE 3. Color Characteristics of Pigments with the Optimal Compositions

Composition	Transition-metal oxides	Chromaticity coordinates		Dominant wavelength, nm	Tone purity, %
		x	*y*		
3	CoO	0.128	0.199	482	49
6	NiO	0.312	0.480	559	40
9	Fe_2O_3	0.520	0.350	585	37
12	Cr_2O_3	0.241	0.575	533	43

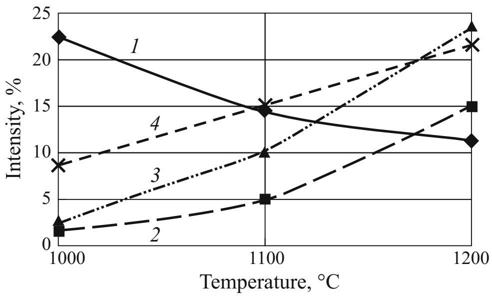

Fig. 1. Variation of the intensity of diffraction peaks of crystalline phases: *1*) SiO_2; *2*) Ni_2SiO_4; *3*) Co_2SiO_4; *4*) cristobalite.

The chemical resistance of pigments is 96.5 – 99.3% to a 1 n solution of NaOH and 96.0 – 98.3% to H_2SO_4.

The phase composition of the synthesized nickel- and cobalt-containing pigments was determined by x-ray phase analysis with a Bruker D8 Advance x-ray diffractometer. It was found that a light-carrying phase, represented by orthosilicate transition metals (Co_2SiO_4, Ni_2SiO_4) and coloring oxides, whose amount decreases with increasing synthesis temperature (Fig. 1), was present. It was also noted that at low heat-treatment temperatures the fluorides decompose and cristobalite is formed only at a higher temperature.

IR-spectroscopy was used to investigate the structural composition of synthesized samples of chromium- and cobalt-containing pigments.

For the spectra of pigment samples containing Cr_2O_3, the vibrational frequencies 300 – 450 cm^{-1} characterize the region of intense absorption by isolated [CrO_6] octahedra. A wide absorption band in the range 860 – 1100 cm^{-1} is present in the spectra of pigments calcined at 1200°C. This band attests to the presence of highly polymerized structural elements with Si – O – Si bands.

Intense absorption is observed in the spectra of the chromium- and cobalt-containing pigments in the wavelength ranges 420 – 470, 760 – 800, and 950 – 1200 cm^{-1}. It is well known that the corresponding band in the spectra of most orthosilicates decomposes into several sections covering a wide range of frequencies (850 – 1000 cm^{-1}), which contains the frequencies of possible vibrations. The stretching vibrations in the range 650 – 800 cm^{-1} indicate the formation of orthosilicates. Thus, the presence of orthosilicates is confirmed.

These investigations have established that it is possible to synthesize ceramic pigments on the bases of silica gel — a waste product from chemical product. The synthesized pigments are characterized by a wide range of colors: green, azure, and brown. It was noted that the brightest pigments are formed when mineralizers (orthoboric acid) are introduced and at synthesis temperature 1200°C.

Enriched quartz sand from the Gomel' Ore-Enrichment Works was introduced, instead of silica gel, into the mix for pigments to be used for decorating ceramic articles. The fact that coloring oxides are capable of forming with SiO_2 colored silicates at relatively low calcination temperature was taken into account. Mineralizers (H_3BO_3, NaF) and modifiers were also introduced into the mixture of sand and chromophore oxides (CoO, NiO, Fe_2O_3, Cr_2O_3).

TABLE 4. Color Characteristics of Synthesized Pigments

Composition	Chromaticity coordinates			Dominant wavelength, nm
	x	*y*	*z*	
3	0.3470	0.3374	0.3156	482
6	0.3701	0.3837	0.2462	570
9	0.3552	0.3424	0.3025	530
12	0.3400	0.3798	0.2802	513

The powders of the initial components were prepared by the traditional technology. The samples were calcined in an electric furnace at temperatures 1000, 1100, and 1200°C with soaking at the maximum temperature for 1 h.

The compositions of the synthesized pigments were identical to the composition presented in Table 1. The color of the pigments, which are similar to those presented in Table 1, varied from very pale blue to deep green depending on the form and amount of transition-metal oxide.

As the synthesis temperature increases, the color of the pigments intensifies. This is probably due to an increase of the amount of light-carrying phases formed. It was found that transition-metal oxides made it possible to synthesize pigments with a wide range of colors: green, light green, brown, blue, and azure. The pigments with optimal compositions (3, 6, 9, 12) are characterized by color saturation, and these pigments calcined at 1200°C were used in subsequent investigations.

Figure 2 displays the dependences of the reflection coefficients of pigments with optimal compositions on the calcination temperature.

Thus, it has been established that the cobalt-containing pigments differ by a saturated azure color, the most pronounced peaks are observed at the wavelengths 550 and 700 nm, which corresponds to the green and red regions of the spectrum; the iron-containing pigments are characterized by saturated brown colors; the chromium-containing pigments are characterized by a saturated green color; the brightest peaks are observed near the wavelengths 450 and 600 nm, which corresponds to the blue and orange regions of the spectrum.

The results of the spectral reflection of the pigments synthesized at 1200°C were used to determine the color characteristics presented in Table 4.

It was confirmed that in the presence of the mineralizer H_3BO_3 and modifier MgO the color of the pigments becomes more saturated. This is due to the formation of a large amount of a light-carrying phase (transition-metal silicates as well as the formation of spinels with the composition MgO · RO (MgO · R_2O_3)).

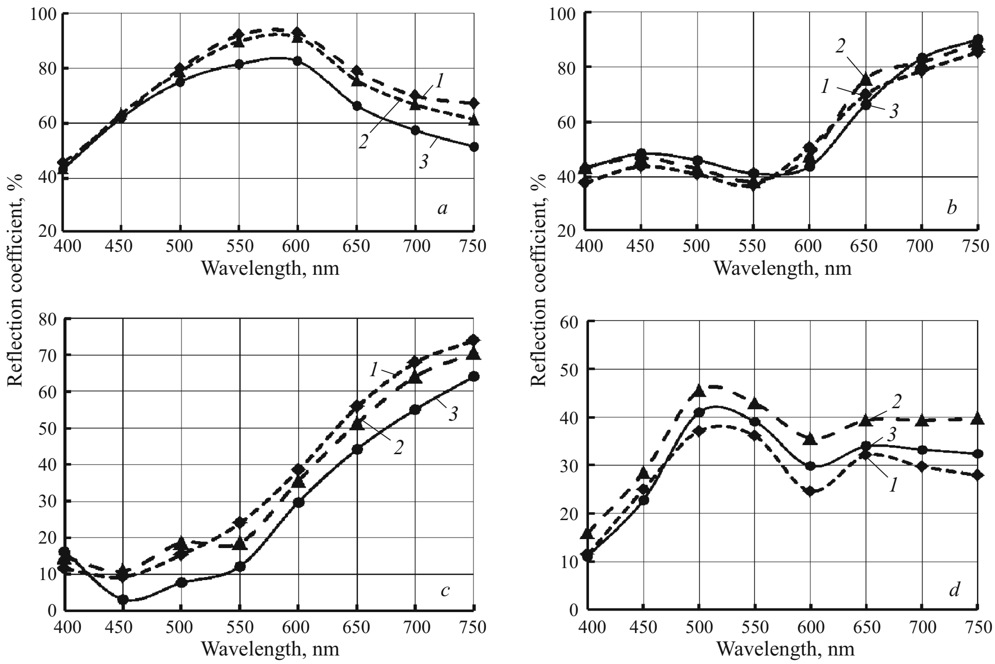

Fig. 2. Spectral reflection curves for nickel-containing (*a*), cobalt-containing (*b*), iron-containing (*c*), chromium-containing (*d*) pigments as function of the calcination temperature: *1*) 1000°C; *2*) 1100°C; *3*) 1200°C.

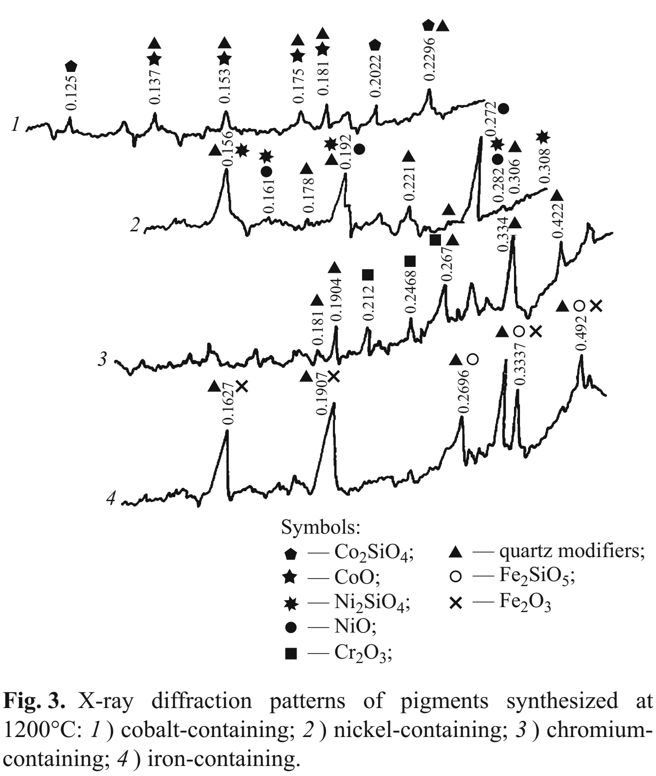

Fig. 3. X-ray diffraction patterns of pigments synthesized at 1200°C: *1*) cobalt-containing; *2*) nickel-containing; *3*) chromium-containing; *4*) iron-containing.

The x-ray diffraction patterns of the synthesized pigments made it possible to detect the formation of a light-carrying phase, represented by Co_2SiO_4. Its greatest amount is found in pigments calcined at 1200°C in the presence of H_3BO_3. Modifications of quartz were also found in addition to Co_2SiO_4 (Fig. 3).

To determine the mechanism by which the cobalt-containing silicate pigments form the change of their phase composition during heat-treatment was examined. Thus, the presence of Co_3O_4 with a spinel-type crystal lattice was recorded at 800°C. The ion distribution in this oxide can be represented as the complex compounds $Co^{2+}[Co_2^{3+}]O_4$. The formation of Co_3O_4, which is black, proceeds in two stages. First, with gradual heating the cobalt oxide interacts with the oxygen in air according to the reaction

$$4CoO + O_2 = 2Co_2O_3.$$

Then Co_3O_4 forms at a higher temperature (700 – 900°C) according to the reaction

$$6Co_2O_3 \to 4Co_3O_4 + O_2.$$

The rhombic compound Co_3O_4 forms only in the temperature interval 1000 – 1200°C. Next the compound decomposes according to the reaction $Co_3O_4 \to 3CoO + 1/2O_2$ and interacts with the silicate base $2CoO + SiO_2 = Co_2SiO_4$. The color-carrying phase represented by cobalt orthosilicate forms.

The light green color is due to the presence of Ni_2SiO_4 and NiO, both of whose reflections are also identified in the diffraction pattern.

The phase composition of chromium-containing pigments is characterized by the presence of cristobalite and chromium oxide. It has been established that additions of H_3BO_3 decrease the amount of cristobalite. The main crystalline phase is represented by Cr_2O_3.

Diffraction peaks belonging to fayalite ($FeO \cdot SiO_2$), α-quartz, and iron oxide (III) were found in the diffraction pattern of iron-containing pigment.

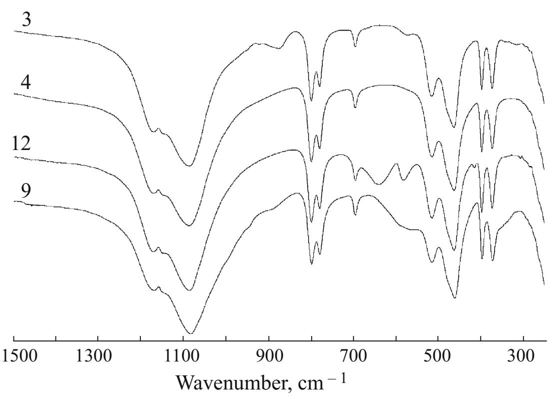

Fig. 4. IR-spectra of pigments synthesized at 1200°C. The numbers on the curves correspond to the composition numbers presented in Table 1.

Intense absorption is observed on the curves of the IR spectra of the pigments (Fig. 4) in the following wavelength ranges: 420 – 470; 760 – 800; 950 – 1200 cm^{-1}. The absorption bands at 464, 697, 795, and 1072 cm^{-1} can be assigned to the spectral lines characteristic for α-SiO_2, whose presence is confirmed by the x-ray diffraction patterns. The stretching vibrations in the interval 650 – 800 cm^{-1} belong to orthosilicates.

Comparing the results of synthesis of pigments based on natural silica and silica gel shows that without mineralizers the silicate formation reactions proceed more actively in mixtures based on natural quartz because of the polymorphic transformation, weakening the Si – O bond, occurring in it. At the initial moment of the pigment-forming reaction in the presence of excess transition-metal ions the weakened bonds rupture in the surface layer of the silica and isolated $[SiO_4]^{4-}$ groups form, which are coupled with one another as a result of the presence of the ions Co^{2+}, Ni^{2+}, Fe^{3+}, and Cr^{3+}.

Initially, the structure of this layer is disordered, amorphous, and then at 1100°C it acquires a more distinct crystalline character. The composition of the silicate pigments formed and the rate and degree of completion of the reaction depend on the ratio, nature, and dispersity of the reactants and impurities.

In summary, when synthesizing pigments on the basis of silica metastable phases are the first to form at the interface, mainly as a result of the diffusion of coloring oxides, whose cations penetrate deep into the SiO_2 particles, breaking the bonds between the groups with the formation of isolated $[SiO_4]$ groups. As temperature increases the structure becomes more ordered and orthosilicates with a more stable form, which is a color-carrying phase in the pigment, appears.

The pigments developed were introduced into glazes and engobes, in the amounts 3 – 5 wt.%, which are used in the production of ceramic tiles for facing walls. The pigments have been successfully tested at the "Keramin" JSC.

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